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Centrally localized ion exchangers as separating sorbents for ion chromatography

Theory and application

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Abstract

The possibility of applying different separation sorbents to those traditionally used in ion chromatography, having the structure of surface-layer ion exchangers, is considered. The theoretical possibility of using a new class of separation sorbents having the structure of centrally localized ion exchangers for highly efficient ion chromatographic separations is shown. The principles of the synthesis of centrally localized ion exchangers and the properties of representative materials, KanK sorbents, are outlined. Examples of the application of KanK sorbents to the analysis of mixtures of anions, metals and ammonium are presented.

1. Introduction

The rapid progress of ion chromatography in analytical chemistry is largely based on successful syntheses and applications of special ion exchangers as packings in separation columns. As a rule, they are fine-grained, narrow-fraction polymeric or silica gel materials, with granules having a thin ion-exchanging surface layer [1]. Such a structure of the separating sorbent grains confers two very important chromatographic properties on the sorbent: a low capacity and rapid kinetics of ion exchange.

The first property permits rapid analysis and the second makes chromatographic separation highly efficient. The separation selectivity is completely determined by the chemistry of the ion-exchange process: by the nature of the functional groups and by the elution power of the mobile phase, which is in no way connected with the special structure of the sorbent particles.

2. Theoretical aspects of selection of separation sorbents

In deciding on a separation sorbent, the basic question is whether the above-mentioned structure of the grains of the so-called surface-layer ion exchanger (SLIE) is necessary for making chromatographic separations rapid and efficient or whether there are alternative ways of achieving these purposes. For example, can the fairly fine fraction of a uniformly localized ion exchanger (ULIE), which finds extensive application in technology, be used or not? Calculations based on the sorption dynamics theory [2] have shown that the nature of the relationships between the packing capacity, its grain size and the efficiency of columns filled with it is such that in order to obtain the necessary characteristics of chromatographic separation of an ordinary series of inorganic anions, a pressure differential of several hundred bars builds up in the separation

columns. Such a pressure destroys polymeric ion exchangers. A decrease in the density of the ULIE functional groups does not change the result because of the proportional decrease in the specific efficiency of the packing (it should be noted that the ULIE capacity can be decreased only to a lower limit of 0.1 mequiv./ml as the further decreases in functional group density generally lead to deterioration of the ion-exchange selectivity [3]). In our opinion, the only way to use ULIE for ion chromatographic purposes is the proposal of Small *et al.* [4] to mix ULIE sub-micrometre particles with large (tens of micrometres) grains of an inert material. It was thus required that the ULIE particles be firmly bonded to the grain surface (Fig. 1). However, can such a packing be considered to be structureless?; it cannot. It has the SLIE structure and this fact considerably lowers the requirements both for the separation system and for the separation conditions needed to obtain the necessary results. Hence our conclusion is not unexpected: the ULIE does not make an efficient separation medium for ion chromatography.

The example cited does not cover all alternatives to separation sorbents of the SLIE type. Let us consider a sorbent characterized by a non-uniform distribution of functional groups located, in contrast to SLIE, not on the surface

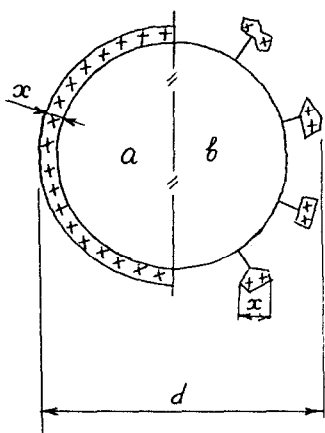


Fig. 1. Structure of surface-layer ion exchangers. (a) Surface-functionalized anion exchanger; (b) agglomerated anion exchanger [4].

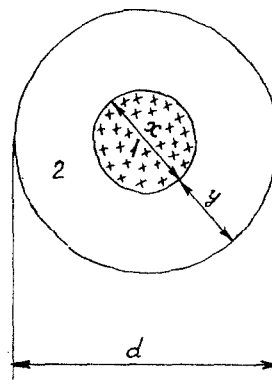


Fig. 2. Structure of centrally localized ion exchangers. 1 = Ion-exchanging nucleus; 2 = inert envelope.

but in the centre of the grains; let us call such a sorbent a centrally localized ion exchanger (CLIE) (Fig. 2). Needless to say, the CLIE inert envelope will be permeable to separated ions and it is desirable that their diffusion through the CLIE envelope be as rapid as possible. In ion chromatography, this sorbent has the general advantage over the ULIE that by decreasing the size of the CLIE ion-exchanging nucleus, it is possible to minimize the ion-exchange capacity and diffusion resistance area in the CLIE grains (it is common knowledge that in ion-exchange materials the diffusion coefficients of ions are several orders of magnitude smaller than in non-ion-exchanging materials having the same porosity [5]). Obviously, a change in the CLIE nucleus size has no effect on the hydrodynamic characteristics of the packing. In other words, conceiving CLIE as an enveloped ULIE nucleus makes it possible to see that CLIE has virtually the same equilibrium and kinetic characteristics at a much lower pressure in the column bed.

The properties of SLIE and CLIE used as packings in separation columns for ion chromatography can be evaluated quantitatively [2]. Based on the structure geometry, for the capacity of these sorbents we have

$$a_{0 \text{ SLIE}} = 6Ax/d \quad (1)$$

$$a_{0 \text{ CLIE}} = Ax^3/d^3 \quad (2)$$

where x is the size of the grain area saturated

with functional groups, A is its local capacity and d is the diameter of a grain. Chromatography uses low concentrations of the sample components compared with those of the eluent. In this area, the ion-exchange isotherms are approximately linear and characterized by constant ion distribution factors Γ_i , which depend on the structural parameters of the grains, similar to the capacity in Eqs. 1 and 2.

To determine which kinetic stage is the slowest and limits the speed of ion exchange in the sorbent grain, the criterion H equal to the ratio of the characteristic times of particle and film diffusion is used:

$$H = \beta_i d^2 / (60 D_i \Gamma_i) \quad (3)$$

where D_i and β_i are particle diffusion coefficient and film diffusion factor, respectively. To large H values there correspond particle diffusion kinetics and to $H \ll 1$ there correspond film diffusion kinetics. In the area of hydrodynamics characteristic for ion chromatography, the film diffusion factor is expressed in terms of ion kinetic constants, α_i , and the linear velocity of the mobile phase, v :

$$\beta_i = \alpha_i v^{0.5} / d^{1.5} \quad (4)$$

where α_i is the well known function of ion charges and equivalent conductivities (ref. 2, p. 28).

Let us find in which kinetic area the SLIE and CLIE work. Assuming that the factor of particle diffusion in Eq. 3 relates only to the size x and the distribution factor is subject to the laws in Eqs. 1 and 2, we obtain from Eqs. 3 and 4 that the criterion H is proportional to the expression $xv^{0.5}/Dd^{0.5}$ for SLIE and to $d^{1.5}v^{0.5}/Dx$ for CLIE. To decrease the capacity, investigators usually try to lower the ratio x/d . For example, for SLIE it is usually ≤ 0.01 . Therefore, film diffusion is characteristic for SLIE and particle diffusion for CLIE. According to this conclusion, the SLIE packed column efficiency (the number of theoretical plates) can be expressed by

$$N_{Bi,SLIE} = 0.5\alpha_i l / d^{1.5} v^{0.5} \quad (5)$$

and the CLIE packed column efficiency is

$$N_{Bi,CLIE} = 30D_i \Gamma_i' l x / d^3 v \quad (6)$$

where Γ_i' is the local distribution factor of the i th ion in the CLIE nucleus, which does not depend on the structural parameters of the grain, l is the separating column length and B and i are indexes.

Analysis of Eqs. 5 and 6 shows that by decreasing d at a fixed x/d it is easier to improve the efficiency for CLIE (the proportionality d^{-2}) than for SLIE (the proportionality $d^{-1.5}$). However, a more detailed analysis of the kinetic dispersion of ion zones in ion chromatography leads to the conclusion about the existence of areas of the chromatographic separation conditions where one or another type of separation sorbent structure has advantages with regard to separation efficiency [2]. In Eq. 6, the efficiency as a function of x/d [at a fixed value of the envelope thickness: $y = (d - x)/2 \neq 0$; Fig. 3] has the maximum at $d = 3x$, which is equal to

$$\max\{N_{Bi,CLIE}\} = 1.11 D_i \Gamma_i' l / x^2 v \quad (7)$$

[$N = 0$ for $x/d = 1$ only when x and $d \gg y$, but this does not mean that ULIE sorbents (with $x/d = 1$) have $N = 0$ because they have $y = 0$]. According to Eq. 2, at this point the capacity is 1/27th of the functional groups density in the CLIE nucleus (A).

The fraction of the feedstock that is chemically modified into SLIE or CLIE is usually made up of particles of various sizes. The functional group

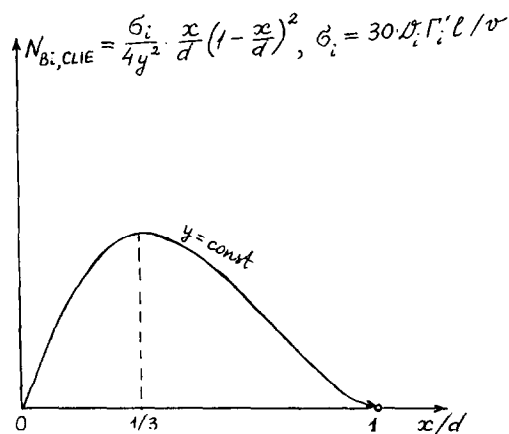


Fig. 3. Efficiency of CLIE bed as a function of x/d [with fixed $y = (d - x)/2$].

bonding required to produce SLIE or CLIE is carried out under the same conditions for the variously sized particles of the feedstock fraction, so the particles of the sorbents synthesized acquire envelopes of equal thickness which, according to Eqs. 1 and 2, results in the individual values of the capacities of the particles being dependent on their diameters (Fig. 4). For SLIE this dependence is a decreasing one and for CLIE it is an increasing one. It has been shown [6] that such dependencies lead to an additional dispersion of chromatographic peaks, which increases with increasing sorbent fraction width. In CLIE this effect is more pronounced. Taking this so-called capacity broadening into account, we obtain the following expression for the efficiency of the separation column:

$$N_{A_i} = N_{B_i} / (1 + \delta a \sqrt{N_{B_i} d / l})^2 \quad (8)$$

where

$$\delta a = |a_0(d_{\max}) - a_0(d_{\min})| / [a_0(d_{\max}) + a_0(d_{\min})]$$

and d_{\min} and d_{\max} are the values of the fraction limits obtained by approximating the particle size distribution by rectangles with height and area corresponding to the distribution. N_{B_i} is determined from Eqns. 6 and 7.

The dependences illustrated in Fig. 4 can be used to identify the sorbent structure and determine the structural parameters of grains. We have used this approach to study the structure of a strongly basic anion-exchanger sulphonation

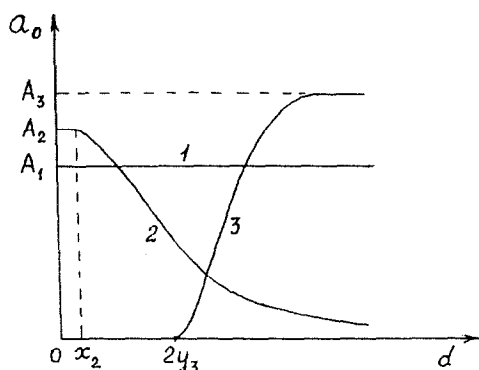


Fig. 4. Dependence of capacity of individual particles on diameter for the various kinds of ion exchangers. 1 = ULIE; 2 = SLIE ($x = \text{constant}$); 3 = CLIE ($y = \text{constant}$).

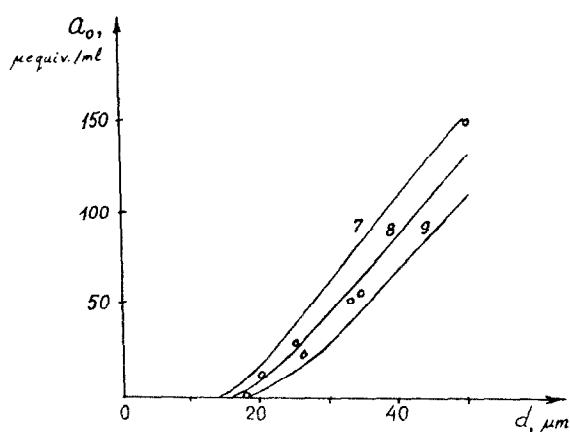


Fig. 5. Dependence of capacity of individual particles on diameter for SAV sorbent. \circ = experimental points; lines = theoretical curves for $y = 7, 8$ and $9 \mu\text{m}$.

product (Sulfirovanniy Anionit Vysokoosnovniy, SAV; Fig. 5). Comparison of the experimental data with Eq. 2 indicated that the experimental conditions permit the production of CLIE characterized by grains not smaller than $16 \mu\text{m}$ and an envelope thickness of $8 \pm 1 \mu\text{m}$.

3. Synthesis of centrally localized ion exchangers

As has been pointed out above, the CLIE grain has, in its centre, a nucleus with ion-exchanging groups, enveloped with a layer of a material inert to the ions being exchanged. The main function of such a layer is, first, to impart to the grain the necessary rigidity and make it sufficiently large to prevent a high pressure build-up in columns; second, to ensure rapid transport of ions to the ion-exchanging nucleus and to distribute uniformly the ionic flow on the boundary between the envelope and nucleus; and third, to decrease the sorbent capacity to the necessary level. The first and third properties develop automatically if the particle of ion exchanger is covered with a polymeric or another, sufficiently strong layer of the necessary thickness, and has no affinity for the ions being separated. To possess the second property, the inert envelope should be a porous hydrophilic membrane. One of the candidates for the CLIE

envelope material is an ion exchanger with polarity opposite to that of the functional groups of the nucleus. For example, if the nucleus is an anion exchanger, a macroporous cation exchanger may be used as the envelope. Obviously, the selectivity of such a bipolar sorbent has two components, the anion-exchanging selectivity of the nucleus and the cation-exchanging selectivity of the envelope. In further discussion of the selectivity of CLIE as an ion-chromatographic separation sorbent, we mean the former component.

In our opinion, the most acceptable of the great variety of ways to synthesize chromatographic sorbents is chemical treatment of the grain surface layer. For example, it is possible to prepare CLIE by taking as the starting material an ion exchanger whose properties allow it to be used as the nucleus and whose grains are of the size necessary for the product and removing the functional groups from the surface layer through the required depth. It should be remembered that the envelope should have the above-mentioned properties.

In developing the CLIE preparation method, we were guided not only by the foregoing considerations, but also by the following facts: (1) strongly basic ion exchangers prepared from a styrene–divinylbenzene (SDVB) copolymer partially lose their capacity with time at temperatures around 100°C; (2) in this temperature range it is possible to sulphonate SDVB with concentrated sulphuric acid; (3) the sulphuric acid neutralizes the quaternary ammonium base split off from the anion-exchanger. In addition, the high viscosity, high boiling temperature and weak dissociation of sulphuric acid in the concentrated state promote the formation of a sharp front of the reaction. The sulphonation reaction front makes a boundary between the nucleus and envelope of CLIE, and therefore the ratio of the nucleus size to the envelope size depends on when the reaction front was stopped.

All the necessary parameters of the product (SAV) synthesis and the means of controlling its properties were found experimentally [7]. On the basis of the procedure for SAV preparation used in this Institute, a series of sorbents (KanK) for

ion chromatography were developed. These sorbents are manufactured by the Sojuz Lyubertsi Research and Production Association (Lyubertsi, Moscow Region, Russian Federation). Russian ion chromatographs (TSVET-3006, KHPI-1: DOKBA, Dzerzhinsk, Nizhny Novgorod Region, Russian Federation) have utilized KanK sorbents since 1989.

4. Applications of KanK centrally localized ion exchangers

4.1. Conventional applications

The KanK sorbents come in three modifications: KanK-ASt, KanK-ASR and KanK-BP. The fraction size varies from 10 to 16 μm and the fraction dispersion is 20–40%. Each of the sorbent modifications is oriented to its own group of ionic mixtures. Thus, KanK-ASt is intended for ion chromatographic analyses of mixtures of medium-retained anions (F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CrO_4^{2-} , PO_4^{3-} , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, etc.). Examples of separations of various mixtures of these anions are given in Figs. 6 and 7. The KanK-ASt

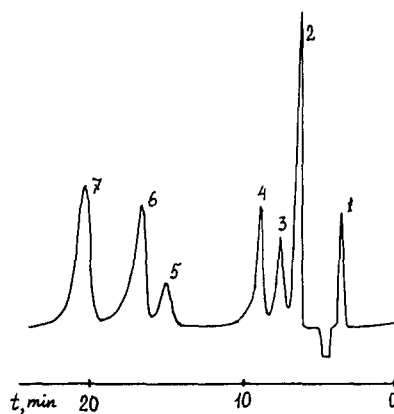


Fig. 6. Typical chromatogram for the separation of an anion mixture. 1 = F^- ; 2 = Cl^- ; 3 = NO_2^- ; 4 = HPO_4^{2-} ; 5 = Br^- ; 6 = NO_3^- ; 7 = SO_4^{2-} (several mg/l of each). Conditions: separation column, 120 \times 5 mm I.D. containing KanK-ASt (15 μm); suppressor column, 200 \times 6 mm I.D. containing Dowex 50- \times 8 (H^+ form); eluent, 2.4 mM Na_2CO_3 –3.0 mM NaHCO_3 –4.0 μM KCNS; flow-rate, 2.3 ml/min.

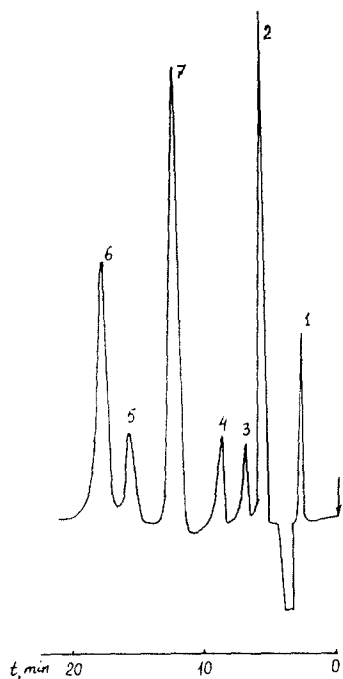


Fig. 7. Reversed separation of the same mixture as in Fig. 6. Conditions as in Fig. 6 except eluent, 9.0 mM Na_2CO_3 –4.0 mM NaOH –5.0 μM KCNS ; flow-rate, 1.7 ml/min.

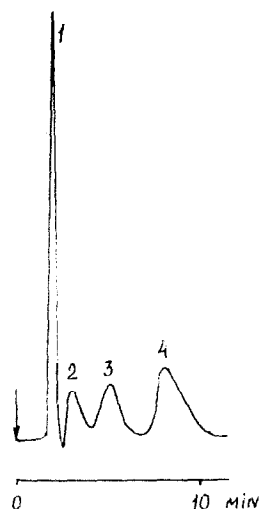


Fig. 8. Typical chromatogram for the separation of a strongly retained anion mixture. 1 = CrO_4^{2-} ; 2 = WO_4^{2-} ; 3 = I^- ; 4 = CNS^- (10 mg/l of each). Conditions: separation column, 120 \times 5 mm I.D. containing KanK-ASR (15 μm); suppressor column, 200 \times 6 mm I.D. containing Dowex 50-X8 (H^+ form); eluent, 3.0 mM Na_2CO_3 –3.0 mM NaHCO_3 ; flow-rate, 1.7 ml/min.

capacity is 5–20 $\mu\text{equiv./ml}$. KanK-ASR sorbent is intended for the analysis of mixtures of strongly retained anions (I^- , SCN^- , ClO_4^- , $\text{S}_2\text{O}_3^{2-}$, CrO_4^{2-} , WO_4^{2-} etc.) (Fig. 8); its capacity is 0.05–1 $\mu\text{equiv./ml}$. KanK-BP sorbent, featuring an increased anion-exchange capacity (100–300 $\mu\text{equiv./ml}$), is intended for the analysis of mixtures of weakly retained anions (HCOO^- , CH_3COO^- , etc. (Fig. 9).

4.2. New applications

Recently, we have developed highly selective methods for the simultaneous ion chromatographic determination of anions and cations, based on the bipolarity of the KanK sorbents. The methods are based on executing selective reactions in two-column anion chromatographic experiments, which convert the cations under study into either non-conducting substances or anions.

The technique of ammonium ion determina-

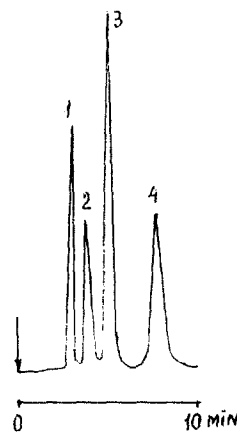


Fig. 9. Typical chromatogram for the separation of a weakly retained anion mixture. 1 = F^- ; 2 = CH_3COO^- ; 3 = HCOO^- ; 4 = Cl^- (several mg/l of each). Conditions: separation column 120 \times 5 mm I.D. containing KanK-BP (15 μm); suppressor column, 200 \times 6 mm I.D. containing Dowex 50- \times 8 (H^+ form); eluent, 1.0 mM Na_2CO_3 ; flow-rate, 2.0 ml/min.

tion uses a selective reaction between ammonium and nitrous acid, forming nitrogen and water molecules [8], and is executed using the H^+ form of the suppressing sorbent. The eluent is selected so that the retention of ammonium ion of the cation-exchanges layer of the KanK-BP separation sorbent and on the sodium form of the Dowex 50 suppressing sorbent was insignificant, but sufficient for resolving the ammonium peak from the water peak. The eluent contains both hydroxide ions to convert most of the ammonium ions into molecular ammonia and nitrite ions to execute the above reaction. Thus, in this technique the suppressing column serves as a postcolumn reactor for ammonium ions. On the basis that the system is anion exchanging, it is also possible to determine the weakly and medium-retained anions (Fig. 10). To perform the rapid routine determination of ammonium ions, sample anions can be separated by ion exchange, which decreases the time of analysis to 2–3 min and permits an analysis selectivity with respect to the other cations of about 100 and an ammonia detection limit of about 0.1 mg/l.

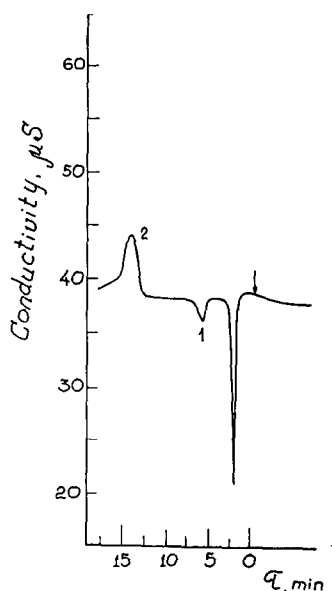


Fig. 10. Chromatogram for highly selective ammonium determination. 1 = NH_4^+ (0.2 mM); 2 = Cl^- . Conditions as in Fig. 9, except eluent, 1.0 mM $NaNO_2$ –4.0 mM $NaOH$ –0.03% formaldehyde; flow-rate, 1.0 ml/min.

Two other techniques are used to increase considerably the selectivity and sensitivity of the determination of metal ions. They may be defined as methods of anion chromatography using controlled on-column conversion of the analyte cations into anions.

The principles on which the methods are based are as follows:

- (1) separation of ions according to the charge sign: stopping of cations and elution of anions;
- (2) injection of a reactant that converts metal cations into anions, in an amount necessary for effecting quantitative conversion of the components under analysis;
- (3) elution of the resultant anions after the sample anions.

The properties that the system must have are as follows:

- (1) the separation sorbent should be bipolar and be highly efficient as regards the separation of anions;
- (2) under the conditions maintained in the separation system, the injected reactants should either form strong anion complexes or oxidize the metal ions to the corresponding oxoanions;
- (3) the eluent should efficiently separate anions and not give rise to rapid metal hydrolysis.

Let us consider the first method, the controlled on-column formation of anionic complexes of metals [9]. One of the most widespread universal complexing agents having a multiply charged ligand, ethylenediaminetetraacetic acid (EDTA), can be used as the reactant. EDTA and transition metals (M^{2+}), such as Pb, Cd, Zn and Cu, form strong doubly charged anionic complexes, $MEDTA^{2-}$. When an excess amount of EDTA is injected into the system, quantitative conversion of metal cations, pre-stopped in the starting layer of the separation column, into anionic complexes occurs. To elute the anions thus produced, and also accompanying sample anions, a carbonate eluent is used. It is distinguished from the usual eluents by containing ammonium ions, which hinder metal hydrolysis (Fig. 11a).

The principle just considered permits the highly sensitive and selective determination of transition metals, which is clearly demonstrated by the

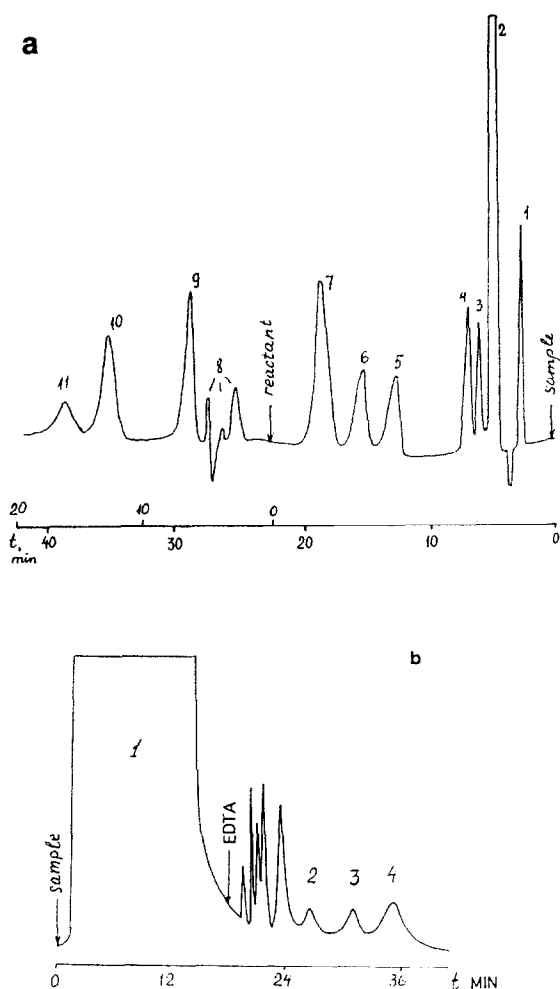
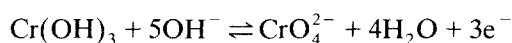


Fig. 11. Simultaneous determination of anions and metal ions. (a) Separation of anion and metal ion mixture. Mixture: 1 = F^- ; 2 = Cl^- ; 3 = NO_2^- ; 4 = HPO_4^{2-} ; 5 = Br^- ; 6 = NO_3^- ; 7 = SO_4^{2-} ; 8 = EDTA; 9 = $CdEDTA^{2-}$; 10 = $ZnEDTA^{2-}$; 11 = $CuEDTA^{2-}$. (b) Black Sea water analysis. 1 = Sample anions; 2 = $Cd + Pd$ ($<2.0 \mu M$); 3 = Zn ($<5.0 \mu M$); 4 = Cu ($<4.0 \mu M$). Conditions: separation column, 120 \times 5 mm I.D. containing KanK-AS t ; suppressor column, 200 \times 6 mm I.D. containing Dowex 50- \times 8 (H^+ form); eluent, 3.3 mM Na_2CO_3 -1.5 mM NH_4HCO_3 -4.0 μM KCNS; flow-rate, 2.0 ml/min; reactant, 5.0 mM Na_2EDTA ; injection volume, 30 μl .

example of a Black Sea water analysis shown in Fig. 11b.

The second method involves controlled on-column oxidation of transition metals to the

corresponding oxoanions. Hydrogen peroxide can be used as the reactant; under basic conditions, it has an oxidation potential of $-0.88 V$, which, in some instances, is sufficient for oxidizing transition metal cations to oxoanions. For example, the oxidation-reduction potential of the reaction



is 0.13, which makes it possible to use the above reagent to oxidize Cr(III) to Cr(VI) in a basic eluent. When 20–40% hydrogen peroxide is injected into the eluent flow, the quantitative conversion of pre-stopped chromium cations into chromate ions occurs. To elute the chromate ions, and also accompanying anions in the solution under analysis, a carbonate eluent of approximately double strength containing a small amount of a weak oxidant is used to neutralize the reducing potential of the separation column. It is convenient to use iodate ion as the oxidant additive.

The difficult task of the separate determination of jointly present forms of chromium can be simply solved with the aid of the proposed method. A sample containing both chromium forms is injected unchanged into a flow of the eluent described above. The ion chromatographic system includes a separation column packed with KanK-AS t bipolar sorbent and a suppressing column packed with Dowex 50 in the H^+ form. The chromium cations are detained by the starting layer of the separation sorbent and the anions, including chromate ions, participate in the chromatographic separation process and their peaks are recorded on the chromatogram. After all the anions have been eluted and the baseline established, the oxidant is injected into the system and quantitatively converts the pre-stopped chromium cations into chromate ions, the peak of which is well resolved from the oxidant anion peaks and is registered together with appropriate retention time counted from the time of injection of the oxidant (Fig. 12). The described method has very good sensitivity and selectivity for the determination of chromium forms in various water solutions.

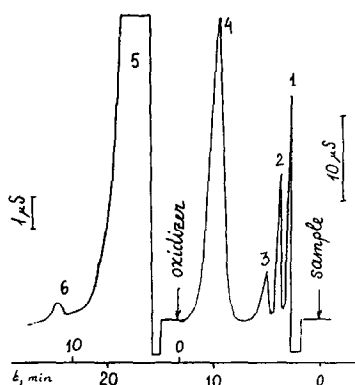


Fig. 12. Determination of different forms of chromium. Mixture: 1 = Cl^- ; 2 = SO_4^{2-} ; 3 = NO_3^- ; 4 = CrO_4^{2-} (12 mg/l); 5 = system peak; 6 = Cr^{3+} (0.5 mg/l). Conditions: separation column, 100×3 mm I.D. containing KanK-ASt; suppressor column, 120×5 mm I.D. containing Dowex 50-X8 (H^+ form); eluent, 5.0 mM Na_2CO_3 -0.22 mM KIO_3 ; flow-rate, 0.9 ml/min; reactant, 20% H_2O_2 ; injection volume, 30 μl . The time scales are plotted with a shift in accordance with injections.

5. Acknowledgement

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